U.S. Environmental Protection Agency

Great Lakes Monitoring

Atmospheric Deposition of Toxic Pollutants

What is Atmospheric Deposition?

Atmospheric deposition occurs when pollutants are transferred from the air to the earth's surface. Atmospheric deposition has been shown to be a significant source of pollutants to the Great Lakes and other water bodies. Pollutants can get from the air into the water through rain and snow, falling particle: and absorption of the gas form of the pollutants into the water.

Why Persistent Toxic Substances are a Problem

EPA monitors levels of PCBs, organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAHs in the air and precipitation of the Great Lakes. These persistent bioaccumulative toxic substances (PBT can accumulate in wildlife, causing reproductive problems and other harmful effects. Many fish in the Great Lakes have high concentrations of these pollutants (thousands or even millions of times higher than levels in the water), making them unsafe for both people and wildlife to eat. In humans, PBTs hav been linked to reduced birthweight, developmental problems in children, neurological problems, and immune system disorders. Many are also suspected carcinogens.

For people, the main route of exposure to these substances is through consumption of contaminated fish and wildlife. For PAHs, but not for PCB: and organochlorine pesticides, inhalation is also an important way that people are exposed. Click on the fish to learn more about levels of toxic pollutants in fish.

- Click here for Information on fish consumption advisories.

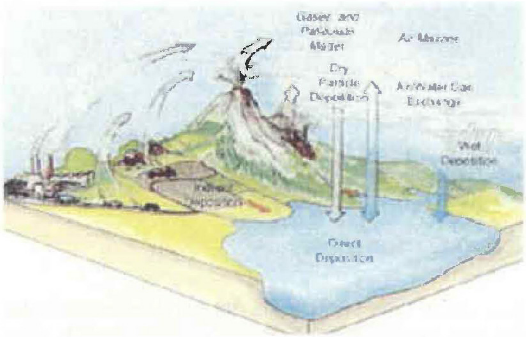
The atmospheric pathway is important for many toxic substances sinc they can remain in the environment long after they have been produc or used. Since these pollutants do not break down easily, they can travel long distances in the air before depositing onto land or water. These chemicals can deposit to the ground or bodies of water, and if i warm enough they can then revolatilize back into the air. This cycle c occur numerous times, with the chemicals traveling to cooler places until the air is not warm enough for revolatilization to occur. This is sometimes called the "grasshopper effect" or global distillation. This is why high levels of PBTs can be found in the cold Arctic, far away from cities and factories.

Types of Atmospheric Deposition

Pollutants are transferred from the air to the water through:

1. wet deposition (rain or snow),
2. dry deposition (falling particles), and
3. gas absorption.

Pollutants may also come OUT of the Lakes through volatilization of gases from the water. Together, g absorption and volatilization are called gas exchange.



EPA and its partners account for wet deposition, dry deposition, and gas exchange in their monitoring. They measure concentrations in rain and melted snow in order to calculate the amour transferred to the Great Lakes through wet deposition. Pollutants on particles are measured determine the amount transferred through dry deposition.

Concentrations of pollutants in the gas form helr determine the amount going into the Lakes through gas absorption. Air and water concentrations are both used to calculate how much volatilizes out of the Lakes. Generally, if the air is cleaner relative to the water, the net transfer of the pollutant will be out of the Lake. If the water is cleaner than the air with respect to that pollutant, the net transfer will be into the Lake. Gas exchange (absorption and volatilization) is the dominant atmospheric deposition process for many semivolatile persistent bioaccumulative toxic pollutants.

The Integrated Atmospheric Deposition Network

Together the U.S. EPA and Environment Canada operate a monitoring network that measures levels o toxic substances in the air of the Great Lakes region. The Integrated Atmospheric Deposition Network (IADN) was created under Annex 15 of the Great Lakes Water Quality Agreement. Samples of air and precipitation have been collected since 1990. Substances monitored by the network include polychlorinated biphenyls (PCBs), organochlorine pesticides, polycyclic aromatic hydrocarbons (PAHs) and trace metals (such as lead and cadmium).

For more information on IADN, see the network website EXIT disclaimer.

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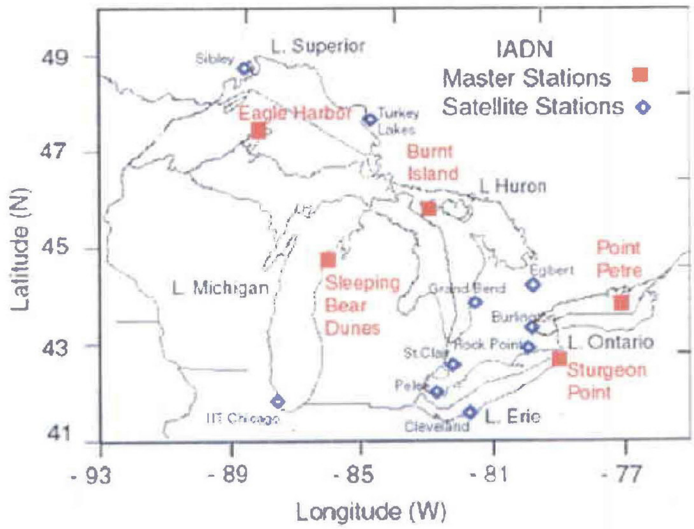

A map of the sampling stations in the IADN is shown above. Five master stations, shown by red square are located in rural areas in order to represent background conditions (i.e., not affected by local pollutic from urban areas) for each of the Lakes. Monitoring of all IADN substances in air and precipitation take place at these stations.

There are also 10 satellite stations, shown in blue. The satellite stations provide additional detail about levels of toxics in the air around the Lakes. All of the Canadian satellite stations are precipitation-only except for Egbert, which monitors in the gas phase only. The U.S. satellite stations, IIT-Chicago on Lak Michigan and Cleveland on Lake Erie, provide the same measurements as those performed at the master stations. The Chicago and Cleveland stations provide useful information about levels of toxic substances in urban air and precipitation. It has been shown that cities have a significant effect on atmospheric deposition of some of these pollutants, particularly PCBs and PAHs, to the Lakes.

Pictures of two master stations are shown below.

View of Lake Michigan from Sleeping Bear Dunes

Sampling platform at Eagle Harbor, on Lake Superior. The rectangular structures on the platform are air-sampling device the precipitation samplers are the two on the left.

High-volume sampler (dry deposition and gas absorption)

The high volume sampler collects pollutants in tl gas and particle forms. A vacuum pump inside tl

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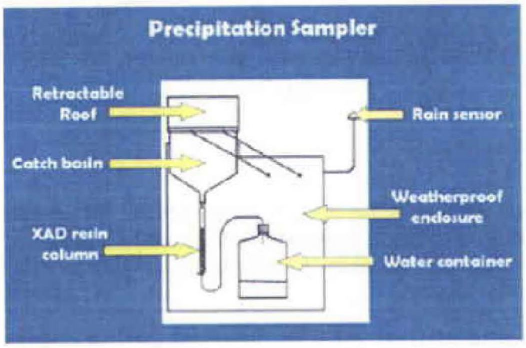
air sampler pulls air through a filter and then through an adsorbent (resin or a foam plug) over a 24-hour period. Both the adsorbent and filter are se to a laboratory for analysis after the 24-hour period is over.

Particles are caught on the filter. The adsorbent captures the pollutants in the gas form. At the laborato the pollutants on the filter and in the adsorbent are measured. The amount of each pollutant on the filte is used to determine the concentration in the air as particles. The amount in the adsorbent tells us the concentration in the gas form in the air. These two concentrations help determine the amount of pollutants transferred into the Great Lakes by dry deposition (particles) and gas absorption, respectivel

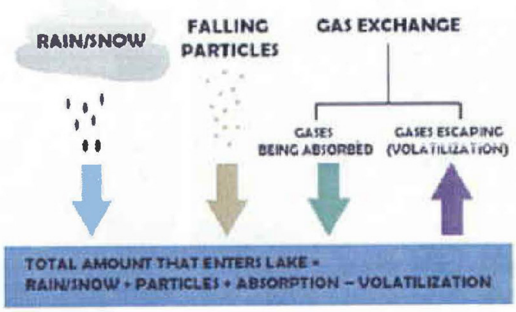
Precipitation Sampler (wet deposition)



When rain or snow falls, a sensor detects the moisture and the retractable roof of the precipitation sampler opens, exposing a funnel-shaped catch basin. Rain and snow fall into the funnel and then through the resin column. The resin captures the pollutants. The water, with the pollutants removed, drains into a container. The volume of water in the container can be measure to determine the amount of precipitation that fell during the one-month sampling period. The amount of each pollutant captured on the resin is determined at the laboratory. (At the Canadian sites, no resin is used and the pollutants are separated from the rainwater in the laboratory.) The pollutant measurement, along with rainfall amounts, is used to find out how much of each pollutant enters the Lakes through precipitation, or wet deposition.

Concentrations and Loadings

There are different ways to look at the impact of these air pollutants-two main pieces of information are concentrations in the air and rain and atmospheric loadings to the Lakes. Concentrations are simply the level of the pollutant found in air or rain (amount of pollutant found in the sample divided by the volume air or rain sampled).



Using the concentrations that IADN measures, w can calculate the total amount of each pollutant transferred from the air to each of the Great Lak for some length of time, usually a year. This is called an atmospheric loading. Here is a visualization of the different ways a pollutant car enter or leave a body of water and how these processes contribute to the total atmospheric loading. As explained earlier, net gas exchange may be positive (into the Lake) or negative (out o the Lake), depending on whether the amount absorbed is greater or less than the amount volatilized from the water. For many PBTs, gas exchange is the dominant pathway of atmospheric deposition. Therefore, the total net loading may also be out of the Lake if enough of the pollutant is volatilized-if the air is cleaner relative to the water. Weather information, the surface areas of the Lakes, and the concentrations of pollutants in the air, rai and lake water are among the factors used to calculate loadings.

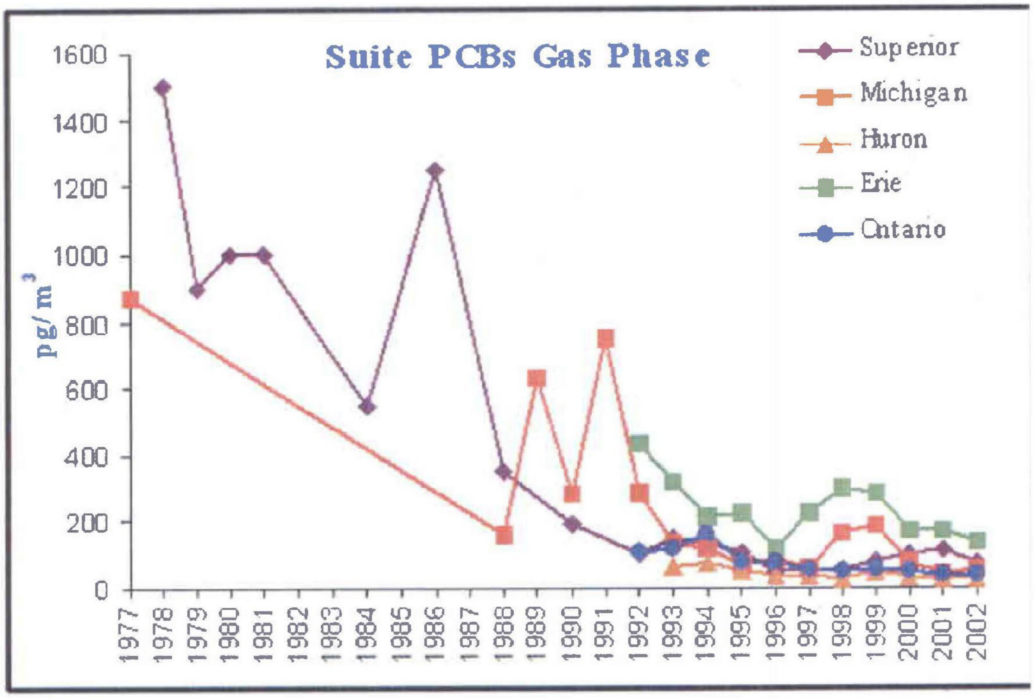
First we will examine the concentrations of these persistent toxic substances over time.

Concentrations

Polychlorinated Biphenyls (PCBs)

PCBs were used widely in the U.S. for industrial purposes, including as lubricants and in electrical equipment, until the late 1970s, when manufacture ceased and uses were severely restricted. Howeve PCBs are still present in older electrical equipment in the U.S. and are still being used in other countrie PCBs can be transported long distances through the air before being deposited.

As shown in the graph below, gas phase concentrations of PCBs in the air have generally been decreasing over time (concentrations from 1991 and earlier are non-IADN data taken from the literature The Lake Erie site station (green line) has consistently shown higher concentrations compared to the master stations for the other Lakes. Further analyses of IADN data have shown that this may be due tc influences from upstate New York and the East Coast (see section on "Using IADN Data to Find Poten Source Regions" below). Urban areas most likely contain more residual sources of PCBs from past usage than less developed areas.

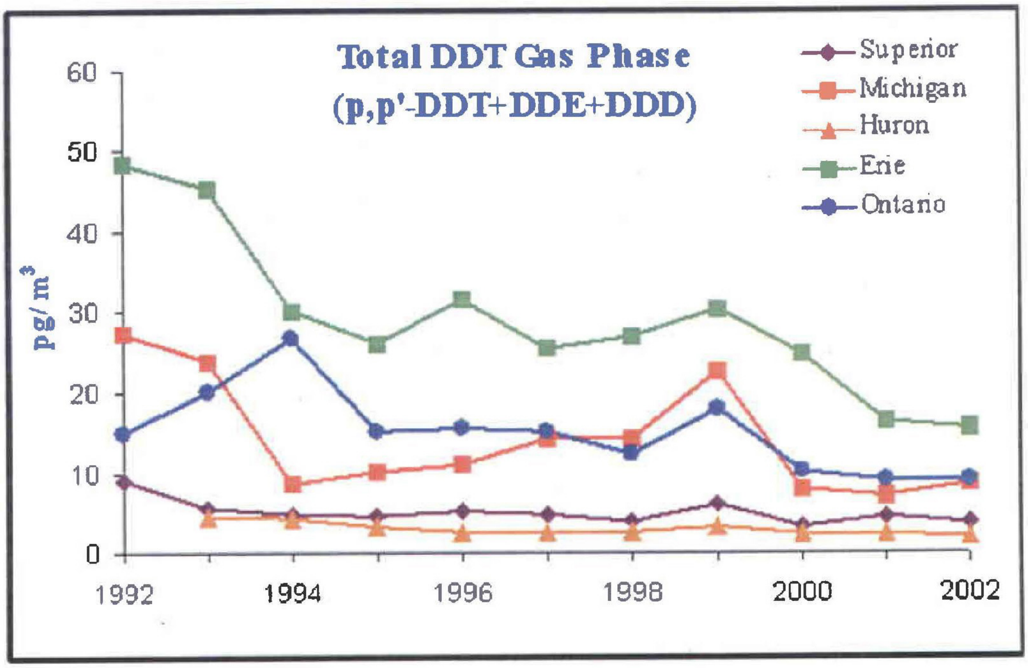


Sources for historical PCB data: Achman et al. 1993; Baker and Eisenreich 1990; Cotham and Bidlem 1995; Doskey and Andren 1981; Eisenreich et al. 1981; Eisenreich 1987; Hornbuckle et al. 1993; Hornbuckle et al. 1994; Manchester-Neesvig and Andren 1989; Monosmith and Hermanson 1996.

Data through 1996 showed a general decline, followed by slight increases for some Lakes during the la 1990s. These increases remain unexplained, although there is some evidence of connections with atmospheric circulation phenomena such as El Nino. More recent data show another decline. Further data will confirm whether levels continue to decline and whether remaining sources of PCBs, including residual sources in the U.S. and long-range transport from other countries, may be contributing to plateauing PCB levels in the Great Lakes region.

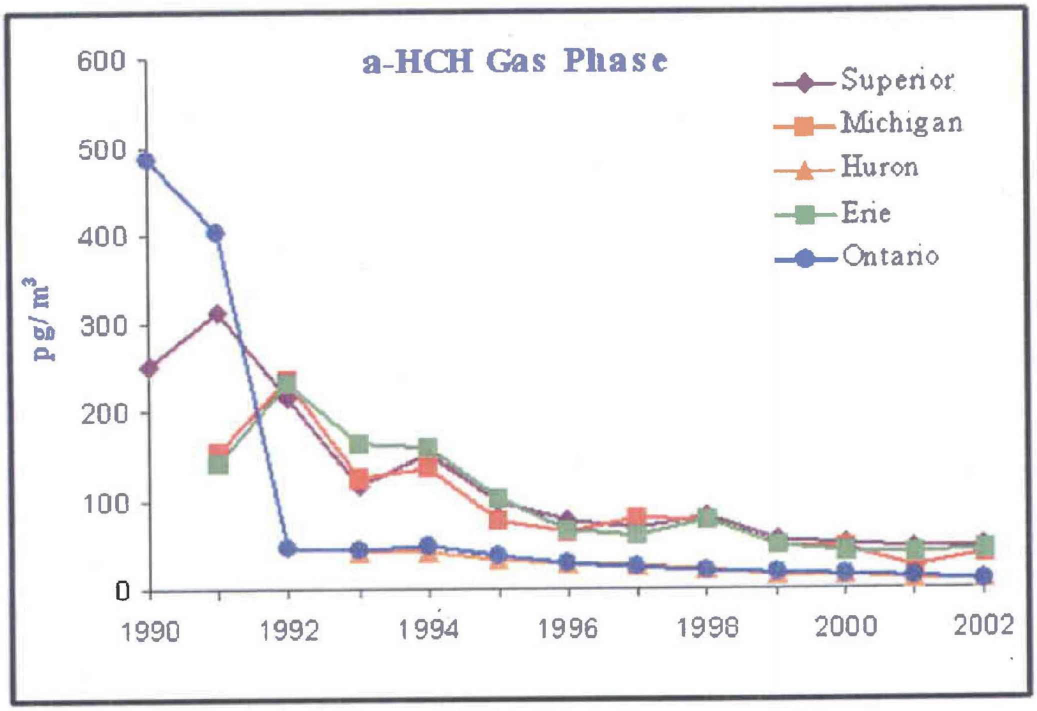
Although levels of PCBs in Great Lakes water have also decreased since the 1970s, current levels can approach or exceed water quality standards for the Great Lakes. PCBs bioaccumulate up the food cha and may reach high concentrations in fish. This has brought about fish consumption advisories in the Great Lakes since PCBs can cause reproductive problems and developmental problems in infants and children.

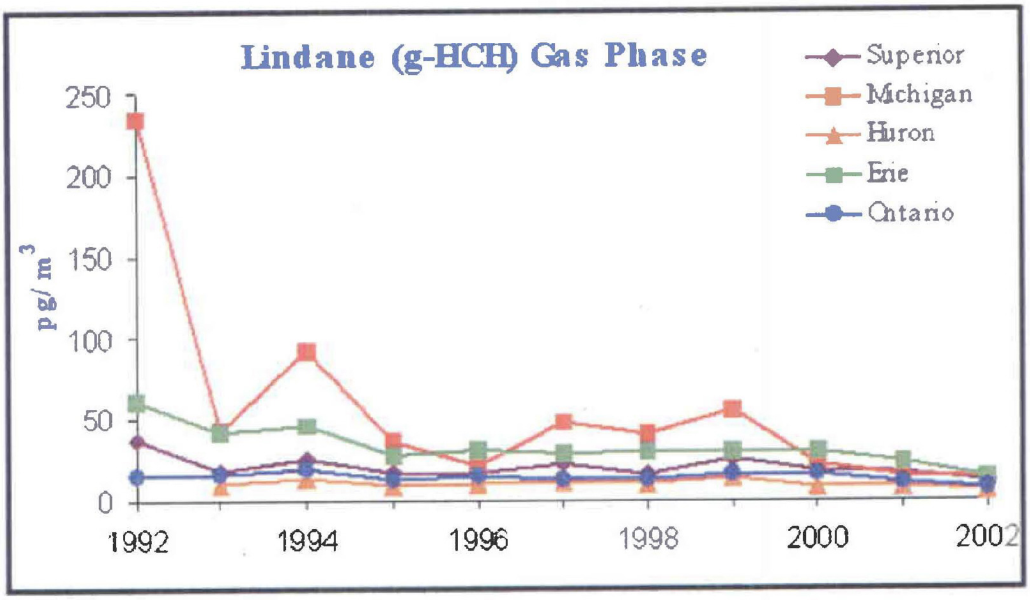
Pesticides



The above graph shows concentrations of Total DDT (DDT plus its breakdown products DDE and DDD over time. DDT was commonly used in the U.S. prior to domestic uses being cancelled in 1972. Agricultural soils once sprayed with DDT, as well as disposal and storage sites, may still offgas DDT ar therefore be a source to the environment. Other parts of the world continue to use DDT in agricultural practices and in malaria-control programs. DDT can travel short or long distances before reaching the Great Lakes. Harmful effects of DDT include liver damage, increased cancer risk, and reproductive problems. DDT was linked to eggshell thinning in fish-eating birds like bald eagles, resulting in hindere reproduction. Many other banned chlorinated pesticides also have adverse reproductive, neurological, immune system, and carcinogenic effects.

Other persistent pesticides monitored by IADN include alpha-HCH and gamma-HCH (lindane). Alpha-HCH was the main component of technical hexachlorocyclohexane (HCH), an insecticide used from th 1940s to the late 1970s, when all uses were cancelled. Lindane was a lesser component of technical HCH, but it continues to be used on its own in the United States, mainly as a seed treatment for grain and feed crops, and all agricultural uses in Canada were cancelled as of the end of 2004.





IADN data show that, in general, concentrations of banned pesticides have decreased since the early 1990s. Even though most of the pesticides monitored by IADN have been banned in the U.S. and Canada, releases to the air may still occur due to emissions from remaining stockpiles, use and production in other areas of the world, and presence in soils where they were once applied and in bottc sediments of rivers and lakes.

Polycyclic Aromatic Hydrocarbons (PAHs)

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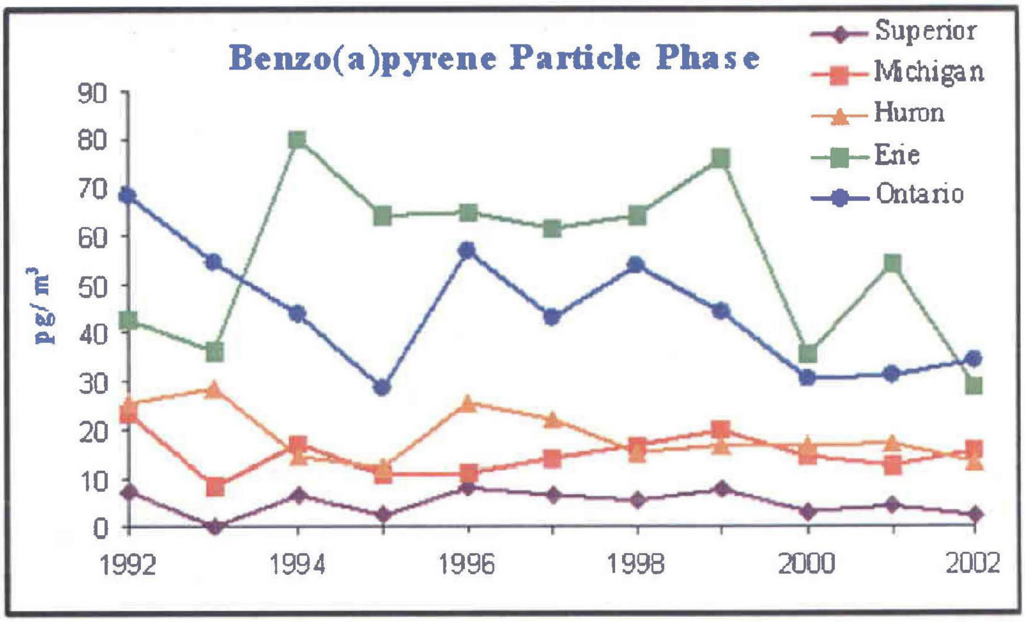
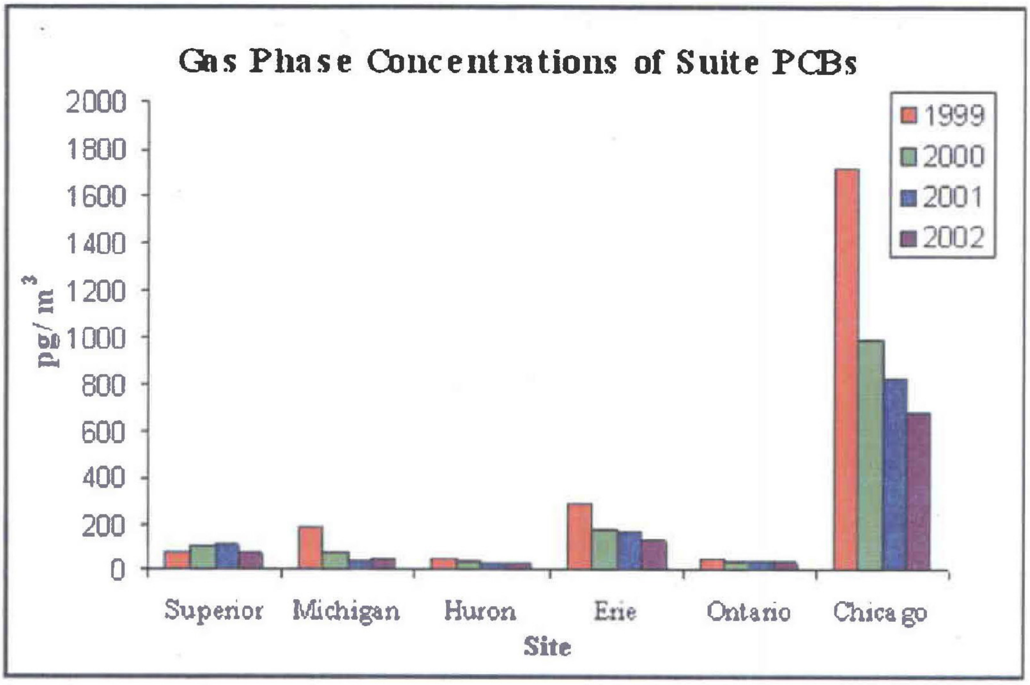


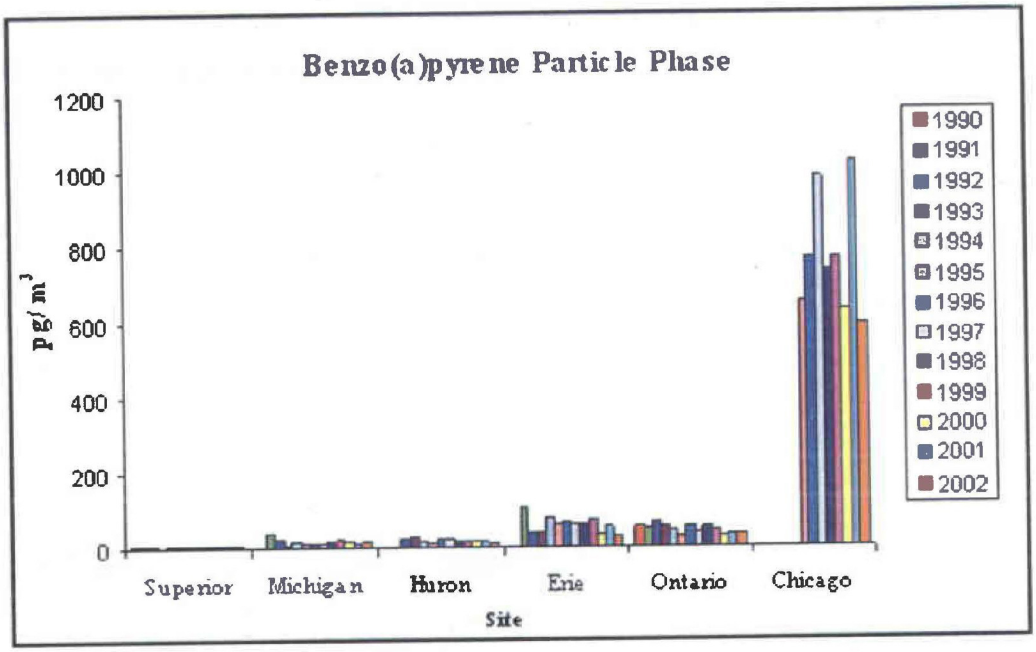
Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds produced during the incomplete burning of fossil fuels, garbage, or other organic substances, such as plant material and meat. They ar usually released in mixtures. Sources of PAHs include cars and factories. They are probable carcinoge and can have other adverse effects.

There has been no consistent trend in concentrations of PAHs. This is shown by the graph of particulat concentrations of benzo(a)pyrene shown above. The lack of a downward trend makes sense given tha PAHs are still emitted in large amounts. IADN data have also shown that lighter PAHs are delivered to the Lakes mainly through gas absorption, whereas heavier ones are deposited on particles or in rain.

The Urban Effect



Data from the IADN satellite site in Chicago show that levels of many IADN pollutants are higher in the city than at the master stations in more remote areas. The graph above shows concentrations of PCBs the gas phase. Concentrations at Chicago are many times higher than at the master stations, represented by Lake names in this graph. For example, PCB levels in Chicago are about 10 times high than at the Lake Michigan master station at Sleeping Bear Dunes, on the northern part of the Lake. Scientific studies have supported this data by showing that rain contaminated by PCBs in Chicago air can increase the amount deposited to Lake Michigan via precipitation by 50 to 400 percent. An EPA study found that the amounts of PCBs entering the Lake through gas absorption increase around Chicago. Rain and gases carrying pollutants from Chicago may increase deposition to the Lake up to tens of kilometers away from the urban area.

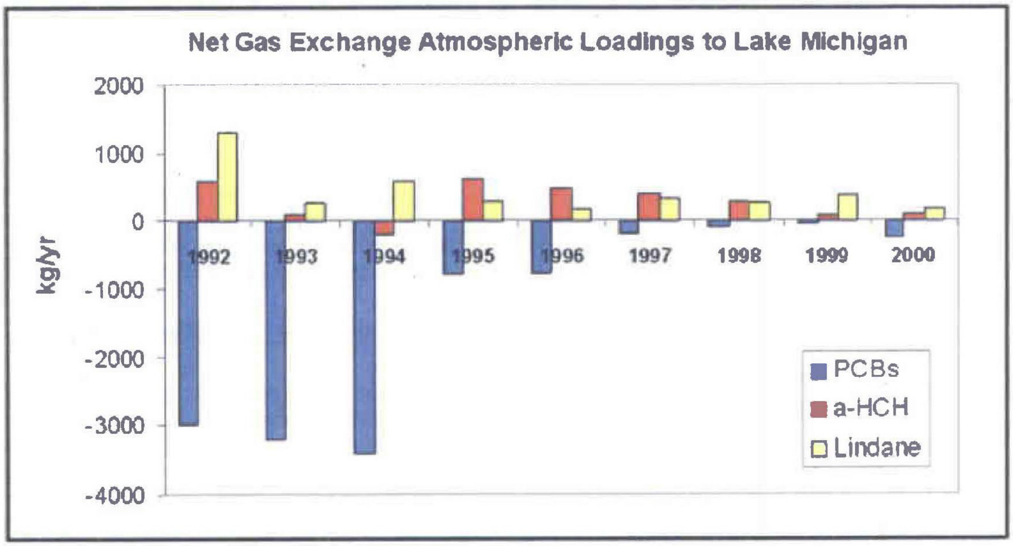


Levels of PAHs are also higher in cities. The graph above shows that concentrations of benzo(a)pyrene on particles are 10 to 100 times higher in Chicago than at the rural master stations.

Next, we'll look at atmospheric loadings to the Lakes.

Loadings

Again, an atmospheric loading is the amount of a pollutant that enters a Lake from the air via gas exchange (absorption minus volatilization), falling particles, and precipitation over some period of time, often a year. IADN data indicate that the net loadings of PCBs and most banned organochlorine pesticides to the Great Lakes are approaching zero (equilibrium). In other words, gas absorption and volatilization are near steady-state, where the amount going into the Lakes equals the amount coming out. The graph below shows net gas exchange loadings (wet and dry deposition are not included) for Lake Michigan for PCBs, a-HCH, and g-HCH (lindane). A bar pointing downward indicates that the net loading is negative, and the compound is volatilizing into the atmosphere. The figure shows that the absolute values of the loadings (the size of the bars) are getting smaller, which indicates that the lake water and the air above it are close to being in equilibrium. When a loading nears zero, this does not mean that pollutant levels in the Lakes are at zero. The pollutants are still present, cycling continuously and evenly between the air and water. In the absence of new sources to the Lakes, concentrations in both air and water, and therefore also in wildlife, will continue to decline.



Source: Blanchard et al. 2004

A new report on atmospheric loadings of PBTs to the Great Lakes has recently been published for data through 2000.

This IADN report states that:

- PCBs continue the trend of volatilizing out of the Lakes but tending towards equilibrium.
- Loadings of banned organochlorine pesticides continue to decline. Current-use pesticides, such as g-HCH (lindane) and a-endosulfan, are still depositing to the Lakes from the atmosphere.
- Loadings of PAHs are positive (into the Lakes) and are not decreasing over time.
- In general, for trace metals (which are monitored in the IADN by Canada only) wet deposition is always more important than dry deposition and there is a lack of trend over time. This is consistent with continuing emissions of trace metals.

For more information on loadings to the Lakes, refer to this report and IADN's other recent loadings reports:

- Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN Results Through 2000
- Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN Results Through 1998
- Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN Results To 1996

Why are these chemicals still around?

Many of these substances do not break down easily. In some cases, they have been banned in the U.S but are still being used in other countries. These persistent chemicals can travel long distances through the atmosphere from other areas of the world. This is called long-range transport. This transport often involves the grasshopper effect (the repeated re-volatilization and deposition of pollutants) described previously.

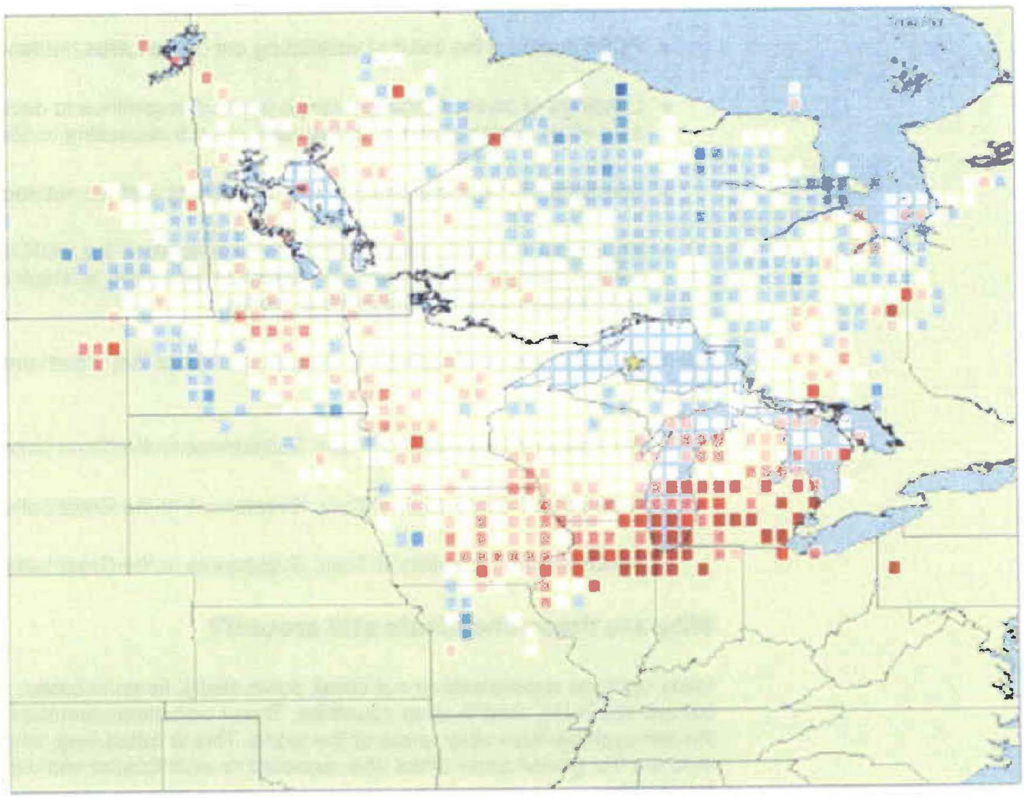
Even though we may have banned a substance, that doesn't necessarily mean it has disappeared. Persistent substances can remain in the environment for decades or longer and cycle between the air, water, soil, and bottom sediments of water bodies. These substances and their breakdown products ca continue to be released into the air for a long time from "reservoir" sources, such as polluted industrial sites and agricultural soils where pesticides like DDT were once applied, both here in the Great Lakes and in other places where they have remained since they were used. As a result, risks to humans and wildlife still exist.

PCBs are still present in older electrical equipment like transformers and capacitors. However, such equipment is being phased out. PAHs and metals are currently emitted by cars and industry, among other sources. Lindane is still used as a seed treatment in the United States. Another pesticide that IAI monitors, endosulfan, is still used in the United States on tobacco and fruit crops.

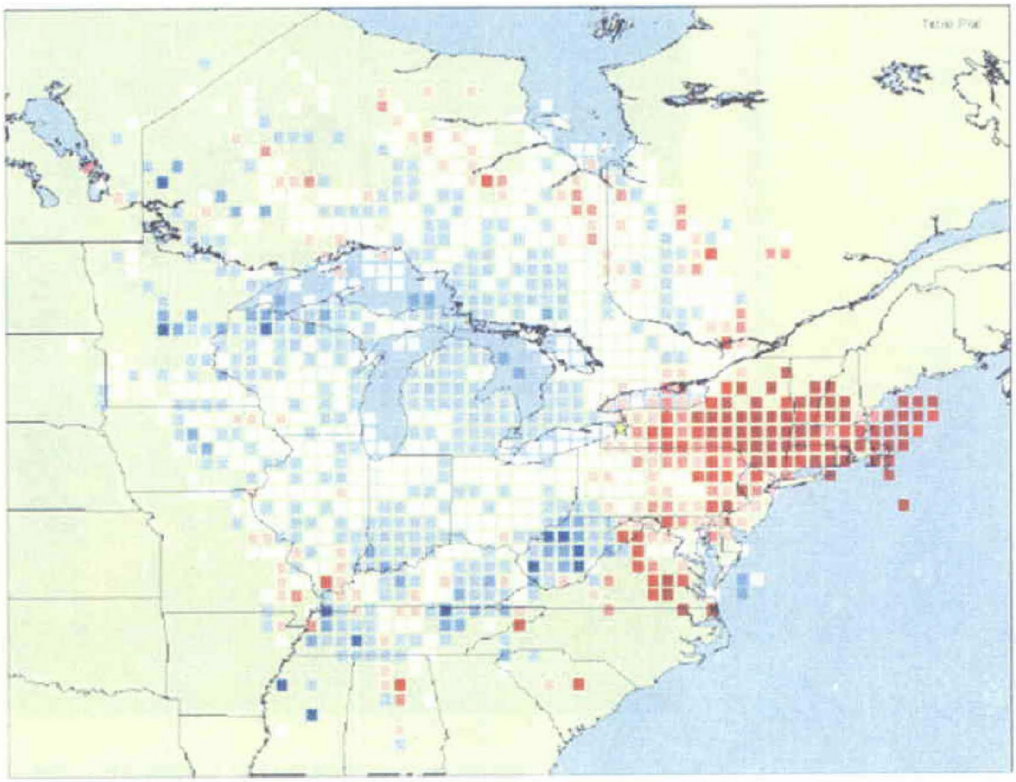
Using IADN Data to Find Potential Source Regions

EPA's partners at Indiana University have used the large database of IADN data to model regions whe some PBTs may be coming from. A National Oceanic and Atmospheric Administration (NOAA) model was used to produce back-trajectories that show where the air that was sampled on a certain day at an IADN station came from. Then the points along those trajectories were mapped using different colors tc show areas where air that produced mostly "dirty" samples (those with higher concentrations of certain pollutants) or mostly "clean" samples (those with lower concentrations) passed through. This produces maps that show potential source areas for different pollutants.

Examples of such maps are shown below. A star indicates the sampling station for which the potential source regions are mapped. The first two maps are for PCBs at two master stations, Eagle Harbor on Lake Superior and Sturgeon Point on Lake Erie. Red and pink squares show areas where more "dirty" trajectories passed through, which are potential source regions.

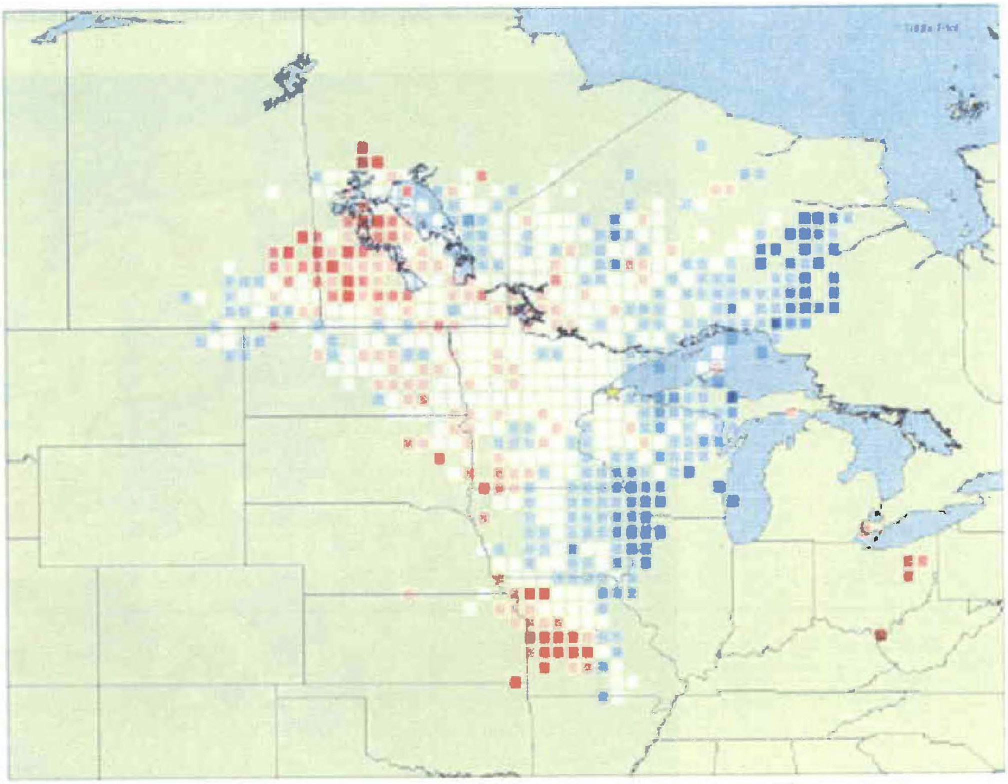


Potential Source Regions for PCBs at Eagle Harbor on Lake Superior



Potential Source Regions for PCBs at Sturgeon Point on Lake Erie

The Eagle Harbor map shows the influence of Chicago-Gary and other urban areas to the south on the air at Eagle Harbor, located on the Keeweenaw Peninsula, which juts out into Lake Superior. Eagle Harbor is located in a relatively rural area. This shows that rural air can be affected by more populated areas located further away. The Sturgeon Point map indicates an influence from the highly populated East Coast of the U.S. The relatively high levels of PCBs found at the Chicago IADN site and past heavier usage of PCBs in cities support the notion that such populated areas could be sources of PCB:



Potential Source Regions for Lindane at Brule River on Lake Superior

Another map shows source regions for lindane (gamma-HCH) for the now-closed satellite station at Bru River, on the western end of Lake Superior near Duluth. As mentioned previously, lindane is still used i the U.S. as a seed treatment for grain and feed crops, but all agricultural uses were cancelled in Canac in 2004. The map shows the influence of the agricultural prairie provinces of Canada and also some influence from farther south in the central U.S. In fact, transport of lindane to the Great Lakes following planting of lindane-treated canola seeds in the Canadian prairies has been demonstrated by modelers from Environment Canada.

These maps do have limitations. The trajectories produced only go back in time 4 days, so influences from further away (such as long-range transport from other countries and regions) cannot be seen. Als a cluster of red squares has more credibility than a single red or pink square.

For more information, consult *Hafner and Hites 2003. Environmental Science and Technology 37(17): 3764-3773.*

Goals

One goal for EPA is to continue to observe declines in concentrations (or for PAHs, to achieve declines in concentrations). Another goal is set out by the U.S.-Canada Great Lakes Binational Toxics Strategy: "virtually eliminate" anthropogenic sources of toxic substances to the Great Lakes. One meaning of virtual elimination is to achieve pollution levels below the concentrations that can be currently be detected using scientific techniques. A study done in the laboratory of Dr. Ron Hites at Indiana Univers estimated that this will take at least decades for banned substances. This assumes that concentrations decline at current rates and that current inputs, including inputs due to long-range transport, do not increase. For substances that are not banned, such as PAHs, further controls are needed to achieve decreases in pollutant levels in the air.

PCBs are still present in old electrical equipment, contaminated sediments and soil, and disposal areas These sources are difficult to pinpoint and are often in urban areas. Efforts are being made to find thes sources and eliminate them, including securing commitments from businesses to remove electrical equipment containing PCBs. In addition, remaining stockpiles of banned pesticides are being collected for proper disposal in "Clean Sweeps" by Great Lakes states. In order to decrease air concentrations o PAHs, better emission controls, alternative fuels and energy sources, and cleaner industrial processes are needed.

Since atmospheric deposition is a major source of these pollutants, reducing levels in the air is a must order for levels to go down in the Great Lakes and in the wildlife that live in and around them.

The Great Lakes Strategy, released in 2002, sets forward 3 key actions for the future of IADN:

1. Integrate IADN with new regional, national, and international monitoring efforts;

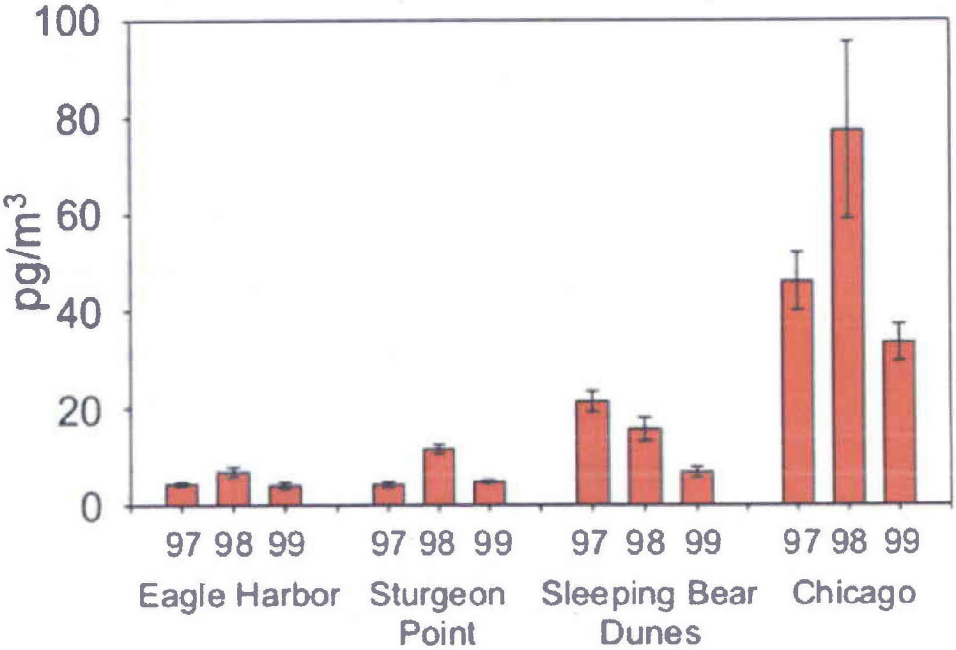
2. Expand at least one U.S. IADN station to include mercury deposition monitoring and evaluate th feasibility and cost of adding additional chemicals of concern to the network, as appropriate;

3. Expand the IADN network to include new urban sites in order to determine urban sources and evaluate current and future regulations.

Efforts to integrate IADN with other PBT monitoring efforts are underway, including via the North American Regional Action Plan on Environmental Monitoring and Assessment. Environment Canada is performing mercury monitoring at its master stations via the Mercury Deposition Network (MDN) and th Canadian Atmospheric Mercury Measurement Network (CAMNet). Monitoring for dioxins and furans is done in Canada through the National Air Pollution Surveillance (NAPS) Network. The U.S. EPA and Indiana University are adding dioxin and furan measurements to the U.S. stations through funding from the Great Lakes Air Deposition (GLAD) program. The Cleveland site was initiated in December of 2002 in order to respond to the third action on urban monitoring.

The IADN is also adding polybrominated diphenyl ethers (PBDEs) to its list of monitored chemicals. PBDEs are used widely as flame retardants in furniture, computers, TVs, and other household items. T European Union banned two types of PBDEs (penta and octa) in 2004, and California has passed a ba on the same two types that will go into effect in 2008. The primary U.S. manufacturer has also agreed t phase out production of penta- and octa-PBDEs.

PBDE data for IADN samples collected during 1997 through 1999 indicate relatively constant levels during that time period. However, an analysis of PBDE concentrations in different parts of the environment (fish, people, etc.) worldwide revealed increasing concentrations that have been doubling about every 4-6 years, with higher levels in North America than in Europe. This implies that air concentrations in the Great Lakes may also be increasing; such a trend would be revealed once more data are collected in the basin. However, once bans go into effect, concentrations may decrease like levels of PCBs and DDT did after bans in the late 1970s and 1980s.



Data courtesy of Hites laboratory, Indiana University. Adapted from Strandberg et al. 2001. Environmental Science and Technology 35 (6): 1078-1083.

Click here to find more information on an Indiana University study on PBDEs in farmed salmon. EXIT disclaimer

For More Information, see:

- IADN Network Website EXIT disclaimer
- U.S. EPA's IADN Resource Page